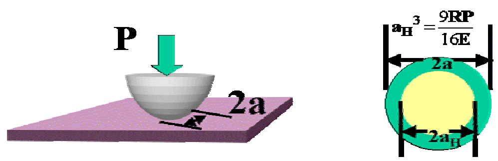
Polymer Multiphase Materials Group

Design of Experiments for High-Throughput Adhesion Mapping

Introduction

Mechanical properties of adhesive bonds are of primary importance to such industries as microelectronics, coatings, and consumer products because they play a critical role in the efficacy of these products in different applications. Experiments based on the Johnson, Kendall, and Roberts (JKR) adhesion test[1] provide quantitative information on the adhesion energy between two materials. Combinatorial methods are a methodology designed to increase knowledge discovery by high-throughput investigations of a large parameter space. For the multi-lens combinatorial adhesion test, a size mismatch exists between the lens array and the combinatorial gradient sample. A drawback to application of this combinatorial technique is the time and computer resources required to measure adhesion across a gradient sample. Design of Experiments (DOE) allows a more efficient, planned investigation of these samples utilizing the JKR adhesion test.



JKR Equation

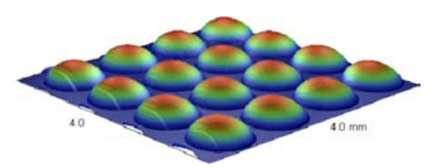
$$a^3 = \frac{9R}{16E}\left[P + 3\pi \mathcal{G} R + \sqrt{6\mathcal{G}RP + (3\pi \mathcal{G}R)^2}\right]$$

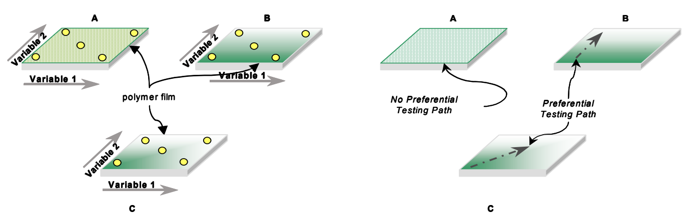
Axisymmetric Adhesion Test

The JKR theory has been widely used to describe the adhesion forces between two surfaces. For this axisymmetric test, a compliant hemispherical lens is brought into contact with a rigid substrate. The load (*P*), displacement (δ) of the indenter and the contact area (a) between the two surfaces are measured. The JKR theory defines the relationship between these experimental measurements and the energy required ($\mathcal{G}$) to either create (loading) or detach (unloading) the interface between these surfaces.

Multi-Lens Combinatorial Adhesion Test

The Multi-Lens technique employs an array of hemispherical lenses to conduct a battery of JKR adhesion tests during one unloading and loading cycle. The size of the lenses ranges from 20 um in diameter and 20 um in height to 1 mm in diameter and 300 um in height. The total number of lenses can range from 1600 to 324, respectively. Unfortunately, this increase in testing efficiency significantly increases the workload and computer resources required to map adhesion across combinatorial samples.

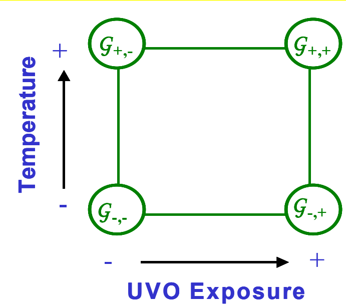




Design of Experiments Procedure

I. For combinatorial adhesion experiments, substrates are prepared with orthogonal linear variations in parameters, e.g. curing temperature and surface energy. Adhesion is measured at a few specific areas to determine the effect of each parameter and any cross interactions between variables on adhesion across the sample.

II. From this initial analysis, the steepest gradient is the focus of future measurements to create a representative adhesion map across the surface.



Factorial Design at Two Levels

For a sample prepared with a gradient in curing temperature (T_- =115 °C – T_+=145 °C) orthogonal to a gradient in UV ozone exposure time (UV_-=30 sec – UV_+=7 min). The equations below determine the effect of each experiment parameter on the work of adhesion[2].

main T effect $= \overline{G}_{T+} - \overline{G}_{T-}$

main θ effect $= \overline{G}_{UV+} - \overline{G}_{UV-}$

T x θ interaction $= \dfrac{\overline{G}_{T+} - \overline{G}_{T-}\big|_{UV+} - \overline{G}_{T+} - \overline{G}_{T-}\big|_{UV-}}{2}$

Factorial Design

The factorial design picture for a sample with two orthogonal gradients. The corners of the square represent the measured variable, e.g. work of adhesion, at the extremes of the investigated parameter space and

Aaron M. Forster, Christopher M. Stafford, Alamgir Karim, and Eric J. Amis

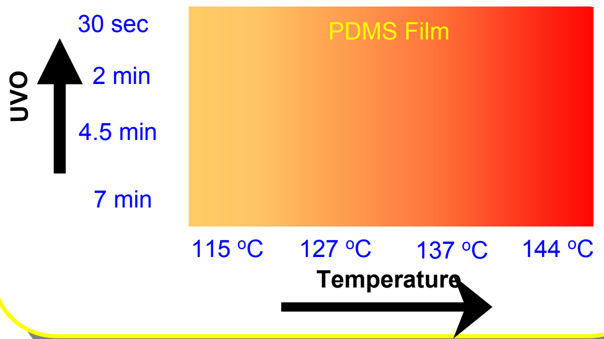
Polymers Division • National Institute of Standards and Technology • Gaithersburg, Maryland

Polymer Multiphase Materials Group

Polydimethylsiloxane Adhesion

Introduction

Polydimethylsiloxane (PDMS) is a model elastomer system used frequently in axisymmetric adhesion tests. The bulk elastic modulus may varied in a gradient fashion by curing on a gradient temperature stage. The PDMS at the low temperature of the gradient undercures over a short time and is more compliant relative to the PDMS at the high temperature. Subsequent exposure of the PDMS surface to a gradient in ultra-violet ozone (UVO) exposure creates a gradient in molecular oxygen content and surface crosslinking across the polymer. As an example of the implementation of DOE in adhesion studies, JKR adhesion tests will be conducted across a PDMS film exposed to orthogonal gradients in curing and UVO exposure



Materials

DOW Sylgard 184 was mixed in a ratio of 15:1 prepolymer to polymer/catalyst and spread across a glass slide. The film was allowed to degas and self-level under ambient conditions for 30 minutes. Next, the film was cured on a temperature gradient (145 °C – 115 °C) for 30 minutes and immediately cooled. *Adhesion was measured across this film with a single glass indenter. DOE used to evaluate the effect on adhesion*. After this measurement, the film was exposed to an orthogonal gradient in UVO exposure time (30 sec – 7 min) and *adhesion was measured across this film and DOE used to evaluate the effect on adhesion*.

Main Effects

I. In the tables to the right, the effect of temperature and UVO exposure on the *work of adhesion* (determined from tack curves[3]) and the *material modulus* (determined from a non-linear least squares fit to loading data) are calculated.

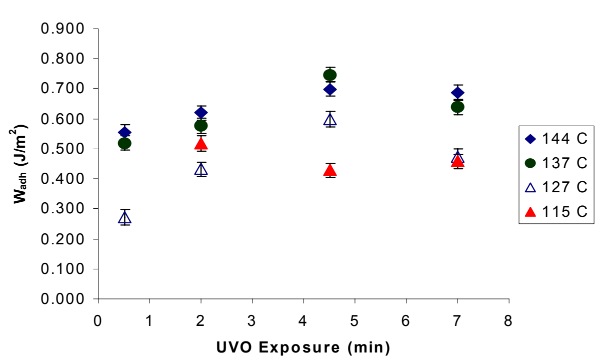
II. From this initial analysis, it is apparent that both temperature and UVO exposure are important to PDMS adhesion to glass. Therefore, future measurements will focus on both of these gradients to create an representative adhesion map across the surface.

Table 1: The effect of *T* and *UVO* on the work of adhesion (J/m²) across the PDMS film as a function of position along the temperature gradient and UVO gradient. The error in the measurement is +/- 0.025 J/m².

	+	-	*Effect*
T	0.62031	0.48764	0.13266
UVO	0.57209	0.41260	0.15949

Table 2: The effect of *T* and *UVO* on the material modulus (MPa) across the PDMS film as a function of position along the temperature gradient and UVO gradient. The error in the measurement is +/- 0.1 MPa.

	+	-	*Effect*
T	2.93	2.32	0.62
UVO	2.79	2.46	0.32



Conclusions

- The preliminary evaluation of adhesion correctly revealed that both temperature and UVO exposure affect adhesion.
- There is a steady increase in adhesion with UVO exposure, until 5 minutes and then a slight decrease. At the lowest curing temperatures, the work of adhesion values are more scattered potentially reflecting surface rearrangement.
- Design of Experiments may be used to simplify the adhesion measurement across substrates encompassing a more complicated parameter space, such as an epoxy film possessing a gradient in curing temperature and an orhogonal variation in crosslinker concentration.

References

1. Johnson, K. L.; Kendall, K.; Roberts, A. D. *Proc. R. Soc. London Ser. A* (**1971**), 324, 301-313 .
2. Box, G. E. P.; Hunter, W. G.; Hunter, J. S.; *Statistics for Experimenters* John Wiley and Sons, Inc.; New York, NY.
3. Work of adhesion taken as $$W_{adh} = \frac{\int_{\delta_{max}}^{\delta_{final}} P\, d\delta}{\pi a_{max}^2}$$ from Crosby, A. J.; Shull, K. R.; *J. Poly. Sci. B* (**1999**), 37, 3455-3472.

Aaron M. Forster, Christopher M. Stafford, Alamgir Karim, and Eric J. Amis

Polymers Division • National Institute of Standards and Technology • Gaithersburg, Maryland